

TRANSLATION

STUDY OF REACTION DIFFUSION IN "METAL-COMPOUND GAS" SYSTEMS
I. GENERAL PICTURE OF PHENOMENON

By V. I. Arkharov and V. N. Konev

August 1960

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1. GENERAL PICTURE OF PHENOMENON

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V. I. Arkharov and V. N. Konev

STUDY OF REACTION DIFFUSION IN "METAL - COMPOUND GAS" SYSTEMS

1. GENERAL PICTURE OF PHENOMENON

1. Rational Basis for Organization of Research on Reaction Diffusion

in Systems Containing Compound Gas

The action of a chemically active gas medium on surface layers of metallic products occurs in two important areas of the industrial practice, such as, firstly, in the chemical treatment in gas media and, secondly, in the service life of products when they are surrounded by aggressive gaseous media, particularly at high temperatures (gas-induced corrosion).

In all these cases, there emerges and develops the process of the so-called reaction diffusion, in which a layer of products resulting from the chemical reaction of metal with gas medium (viz. the dross) appears on the outer surface of metal; a further process of their interaction is effected by the diffusion of atoms or ions of metallic and gaseous components through the layers of produced solid phases, combined with chemical reactions in boundary zones near surfaces separating "metal - dross" and "dross - gas medium", as well as on boundaries between layers of reaction products - phases (differing in composition), when several of them are developed.

Numerous researches were conducted in this important area of physico-chemical problems. Refraining from their detailed review, we can note that these researches were concerned mainly with examining

the processes of reaction diffusion in binary "solid metal - gas" systems, whose both components are chemical elements. We can refer also to numerous researches of the same kind for more complex systems of the "solid alloy of metals - gas" type, in which several chemical elements (alloy components), interacting with one gaseous element, participate on the side of the initial solid medium¹.

Of course, the studies of these systems are more interesting from the viewpoint of practice in which the alloys are employed almost constantly instead of pure metals; however, at the same time, they are more difficult for researches than the binary systems. But, if practical interests are discussed, we must note that the practical requirements complicate still further the researches on reaction diffusion, because of an ever-increasing number of cases encountered in practice, wherein not only the initial solid medium but also the gaseous medium contains several chemically active components included in the composition of developed, dross-layer forming solid phases. Thus, for instance, parts of equipment in some branches of engineering experience the action of fuel-combustion products, containing (in addition to residual oxygen) also the components which yield, from the gaseous phase, sulfur, carbon and other elements participating in the dross formation; besides oxygen, also nitrogen, etc., turn out to be

¹ Here we may include also the cases wherein the gaseous medium contains, apart from an active chemical element, likewise other neutral elements, i. e. those not comprised in the composition of chemical compounds produced on the surface of metal.

chemically active for certain metals and alloys during their oxidation in atmospheric air.

The multicomponent nature of the system causes a complication of the reaction-diffusion process in two respects.

Firstly, an increase in the number of system components results in a growing variety of nascent intermediate phases in this system; these phases differ in composition and structure, which complicates decoding of the cross-construction picture.

Secondly, variation in the diffusion penetrance of intermediate phases, caused by differences in their structure and composition, induce variations in the total course of diffusion through the entire multilayer cross upon the whole, i. e. complicate the picture of reaction-diffusion kinetics.

In formulating the general goal of studying the reaction diffusion (particularly, the gas corrosion and technological processes involved in production of heat-resistant coatings) for seeking practical methods to regulate these processes, it is possible to establish a large group of more special problems which may be described as problems of studying the reaction-diffusion mechanism in systems belonging to the type of 'solid element (metal) - mixture of two chemically active gaseous components' (in the presence or absence of other neutral gaseous components). For the sake of brevity, such systems can be designated by the symbol $\omega_2 = (X^1 + X^2)^2$. Translator's note: footnote² appears on the next page of this translation.

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We assume that X' and X'' do not interact in the gaseous phase and, consequently, do not produce gaseous compounds of the $X'_2 X''_2$ type, whose interaction with metal may differ from the interaction of X' and X'' with metal.

2. Factors Determining Formation of Structure in Diffusion Layers and Kinetics of Reaction Diffusion in Systems of "Me - (X' + X'')"-Type

a. Significance of the type of state diagrams for binary and ternary systems of elements participating in the reaction diffusion.

The phases which may develop in the constitution of dross during a reaction diffusion in the "Me - (X' + X'')"-system, as well as the chemical composition and the crystalline structure of these phases, are determined, first of all, by the state diagram of the ternary Me - X' - X'' system; ternary chemical compounds, developing in dross, are contained in this diagram and they emerge on a simultaneous diffusion of X' and X'' elements, adsorbed from the gaseous medium on the surface of the solid phase and into the depth of the latter, where diffusing atoms (or ions) of X' and X'' encounter the atoms (or ions) of Me. The chemical interaction of three components will form, at the same time, a dross with a diverse phase composition, according to differences in the character of pseudo-binary state diagrams produced by chemical compounds which are contained in binary systems of "Me - X'" and "Me - X''".

We shall examine three principal cases of a various combination of these compounds, i. e. principal types of such pseudo-binary systems that correspond to principal variants of the reaction-diffusion process in "Me - (X' + X'')³" systems. We shall assume, at the same time, that everyone of constituent binary systems, Me - X' and Me - X'', contains one chemical compound, Me_mX'_n and Me_pX''_q, respectively.

First Case. The pseudo-binary state diagram with the unlimited reciprocal dissolvability of compounds produced in binary systems of Me - X' and Me - X''. /214

During the conjunct reaction diffusion of X' and X'' elements into the solid metal Me we shall have a formation of dross consisting of one phase with gradients of the concentration in depth for both components. The composition of this phase can be designated conventionally by the formula

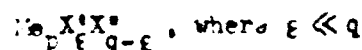
$$[\xi(\text{Me}_m\text{X}'_n - \alpha), \eta(\text{Me}_p\text{X}''_q - \beta)], \text{ where } \xi + \eta = 1,$$

wherein ξ/η depends on the relation of partial pressures of X' and X'' in the gaseous medium, and on the degree of the chemical affinity of these elements to metal; α and β vary from minimum values on the outer surface of dross to maximum values on the dross-metal boundary; at the same time the relations $\alpha \ll n$ and $\beta \ll q$, are retained.

³ In the presence of a large number of intermediate phases in binary systems, the analysis of a role played by various combinations of types of such systems in the general reaction-diffusion process requires taking into account a correspondingly large number of state diagrams of pseudo-binary systems of the "Me_mX'_n - Me_pX''_q" type.

In a special case, when only solid solutions of X' or X'' in Me are produced in constituent binary systems, i. e. (Me, X') and (Me, X'') , the dross will consist of the ternary solid solution.

Second Case. The pseudo-binary state diagram with a limited dissolvability of X' and X'' in $Me_pX'_n$ and $Me_qX''_q$ compounds. Here the dross structure will have another form; the outer layer will consist of the phase with a higher content of this particular element (X' or X'') which is endowed with a lower diffusion mobility. If we assume that the diffusion mobility of X' is lower than that of X'' , then the outer layer will consist of the phase $Me_m(X'_{n-\delta}X''_{\delta})$, where $\delta \ll n$. At a specific depth in the dross, there is a possibility of emergence and development of a layer of another phase with an increased concentration of this particular "gaseous" element which is endowed with a higher diffusion mobility, viz. the phase



(for the example presented above).

Third Case. No dissolvability of X'' in $Me_mX'_n$ and of X' in $Me_qX''_q$.

In this case, the difference in the chemical affinity of X' and X'' to Me plays a principal role in the formation of dross structure. At the very beginning, there develops on the metal surface a layer composed of the phase existing in the binary system which is produced by Me with this particular element (either X' or X'') that has a closer chemical affinity to Me , say, for instance, with X' (i. e. the layer consists of the $Me_mX'_n$ phase). Due to the fact that the other element (X'')

is not dissolvable in this layer, the latter prevents X^* from penetrating to the metal and from producing compounds present in the second binary $Me - X^*$ system, although these compounds are thermodynamically stable under conditions of the process, similarly to compounds in the $Me - X'$ system.

b. Significance of the type of the crystalline structure of phases produced in the dross.

The above exposition makes it clear that differences in the rate of diffusion of components through the layers of phases - reaction products are very important for the dross formation; at the same time, these differences become established to a different extent for various layers of the dross; accordingly, a more or less complex distribution of the depth concentration of components in the dross becomes established. In turn, the diffusion rate of components is determined by crystallochemical characteristics of produced phases, such as the crystallographic type of lattices; character and magnitude of forces of the interatomic bond in these lattices; ratios of atomic and ionic radii of components;

tendency of phases to the development of vacancies; relative dimensions of interstices and atoms; types of the solid solution of X' and X^* components in the lattice of the chemical compound and, in particular, the type of the solid solution produced by a more rapidly diffusing component (for instance, X^*) in the lattice of compound of a less slowly diffusing component (X') with metal, i. e. in the lattice of $Me_m X_n'$ phase, which constitutes in the given case the outer layer of dross. In addition

to these principal factors, there are some secondary factors, depending on principal ones, which are highly important for the diffusion in solid phases. These secondary factors include the continuously stable distortions of structure; mosaic nature and substructure of crystallites; the presence of intercrystallite bondings in polycrystals, etc.

The crystallographic type of lattices and the character of bonding forces in these lattices determine also the mechanism of these solid-phase chemical reactions (phase transformations) which occur during the reaction-diffusion process on boundaries of dross layers. A special place in this group of phenomena, constituting the reaction diffusion, is occupied by the chemical adsorption of gaseous components on the outer surface of the dross.

The necessity of a detailed study of the dross structure upon the whole, and of the structure of its individual constituent homogeneous layers, is caused by these considerations⁴.

⁴ In addition to the above indicated factors, viz. the phase composition and structural relation of the diffusion in each single-phase layer of dross, in order to gain an understanding of kinetics of the reaction diffusion upon the whole, it is necessary to take into account a number of supplemental factors, particularly phase transformations in metal when X' and X'' elements (or one of them) dissolves in this metal, thus changing the conditions and rate of the chemical reaction on the metal-dross boundary; further on, in some cases it is necessary to take into consideration the possibility

of the formation of solid phases, resulting from chemical reactions in the gaseous medium, on the surface of metal (or dross). This can delay the penetration of X' and X'' atoms into the dross, or the exit of Me atoms (diffusing from inside) on the outer surface of the dross. This may change also the structure of dross, inasmuch as its outer layer will become subject to changed thermodynamic conditions due to a different concentration of X' and X'' on the outer surface of dross.

Ural State University

Named in Honor of A. M. Gorkiy

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